L6 ANSWER 12 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 118:102236 CASREACT <<LOGINID::20080513>>

TITLE: Preparation of aryllithiums in C6 dialkyl ether

solvents

INVENTOR(S):
Morrison, Robert Charles

PATENT ASSIGNEE(S): FMC Corp., USA

SOURCE: PCT Int. Appl., 21 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT	NO.	KIND	DATE		APPLI	CATION N	o. :	DATE			
											
WO 9219	622	A1	19921112		WO 19	92-US120	8	19920	214		
W:	AU, BB,	BG, BR	, CA, CS,	FΙ,	HU, JP,	KP, KR,	LK,	MG,	MW,	NO,	RO,
•	RU, SD										
RW:	AT, BE,	BF, BJ	, CF, CG,	CH,	CI, CM,	DE, DK,	ES,	FR,	GΑ,	GB,	GN,
	GR, IT,	LU, MC	, ML, MR,	NL,	SE, SN,	TD, TG					
AU 9219	262	A	19921221		AU 19	92-19262		19920	214		
PRIORITY APP	LN. INFO	. :			US 19	91-69243	8	19910	429		
					WO 19	92-US120	8	19920	214		

OTHER SOURCE(S): MARPAT 118:102236

Thermally stable solns. of aryllithium compds. were prepared by reaction of Li dispersions with monohaloaryl compds. in solvents ROR1 (R, R1 = C3-8 alkyl; ≥6 carbons total) with a molar ratio of ether/monohaloaryl compound of ≥1.5 at a temperature of 5-65°. Thus, 1 equiv PhCl was added dropwise to a stirred slurry of Li in 1.8 equiv BuOBu followed by a postreaction period and filtration to give a .apprx.25% solution of PhLi which was stable for ≥40 days at 20-22°.

RX(1) OF 1

$$\begin{array}{c|c} C1 & \\ \hline & \underline{Bu20} \end{array} \begin{array}{c} Li \\ \hline \end{array}$$

968

NOTE: product has improved stability in this solvent

L6 ANSWER 8 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 127:5187 CASREACT <<LOGINID::20080513>>

TITLE: Preparation of aryllithium in ether solutions using

Lewis bases

INVENTOR(S): Schwindeman, James A.; Sutton, Douglas E.; Morrison,

Robert C.; Stryker, Sonia S.

PATENT ASSIGNEE(S):

SOURCE:

FMC Corp., USA U.S., 4 pp. CODEN: USXXAM

DOCUMENT TYPE:

Patent

LANGUAGE:

English

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

	PAT	CENT	NO.		KI	ND	DATE			A	PPLI	CATIO	ои ис	ο.	DATE			•
	US	5626	798		Α		1997	0506		U:	S 19	96-58	8781	3	1996	0105		
	WO	9725	334		A	1	1997	0717		W	0 19	96-U	S762	4	1996	0524		
		W:	AL,	AM,	AT,	AU,	AZ,	BB,	BG,	BR,	BY,	CA,	CH,	CN,	CZ,	DE,	DK,	EE,
			ES,	FI,	GB,	GE,	ΗU,	IS,	JP,	ΚE,	KG,	KΡ,	KR,	ΚZ,	LK,	LR,	LS,	LT,
			LU,	LV,	MD,	MG,	MK,	MN,	MW,	MX,	NO,	ΝZ,	PL,	PT,	RO,	RU,	SD,	SE,
			SG,	SI,	SK,	TJ,	TM,	TR,	TT,	UA,	UG,	UZ,	VN					
		RW:	ΚE,	LS,	MW,	SD,	SZ,	UG,	ΑT,	BE,	CH,	DE,	DK,	ES,	FI,	FR,	GB,	GR,
			IE,	ΙΤ,	LU;	MC,	NL,	PT,	SE,	BF,	ВJ,	CF,	CG,	CI,	CM,	GΑ,	GN,	ML,
			MR,	ΝE,	SN,	TD,	TG											
	· AU	9658	036		Α		1997	0801		Α	U 19	96-58	8036		1996	0524		
	DE	1968	1729		T	0	1998	1217		D!	E 19	96-19	9681	729	1996	0524		
	DE	1968	1729		C	2	2000	1116										
PRIC	RIT	APP	LN.	INFO	.:					Ü	S 19	96-58	8781	3	1996	0105		
										W	0 19	96-U	S762	4	19960	0524		

OTHER SOURCE(S): MARPAT 127:5187

An improved process for producing high purity solns. of aryllithium compds. and the product solns. are claimed. The process comprises reacting a particulate alkali metal having a particle size of 10-300 μm, with an aryl halide in a normally liquid ethereal solvent ROR1, wherein R and R1 are selected from the group of alkyl radicals containing from 3 to 6 C atoms, in the presence of a Lewis base selected from compds. of the formula: R2AR3(R4)z and cyclic -(CR5R6)y-(A(R4)z)- wherein A is selected from O, N, P or S; R2, R3, and R4 are selected from alkyl radicals containing from 1 to 6 C atoms; R5 and R6 are independently selected from H or alkyl radicals containing one to six C atoms; y = 4 to 6; but when A is O or S, z = 0; and when A is N or P, z = 1, and provided there is a mole ratio of ether to aryl halide of at least 1.3 to 1 and a mole ratio of Lewis base to aryl halide of from 0.01 to 0.5. For example, to a reaction flask containing 1.25 mol Li powder and 0.94 mol Bu2O was added, dropwise, over a period of 60 min, a solution of 0.52 mol PhCl and. 0.052 mol MeOtBu, while maintaining the reaction temperature at 30-35°; the yield of PhLi was 87.4%. If no MeOtBu was present, the yield was 80.8% and the reaction was slower (16% PhCl remaining after 120 min vs. 6%).

RX(1) OF 1

L6 ANSWER 10 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 123:228304 CASREACT <<LOGINID::20080513>>

TITLE: An efficient procedure for the synthesis of C-chiral

bisphosphines

AUTHOR(S): McKinstry, Lydia; Livinghouse, Tom

CORPORATE SOURCE: Dep. Chem. Biochem., Montana State Univ., Bozeman, MT,

59717, USA

SOURCE: Tetrahedron (1995), 51(28), 7655-66

CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Pergamon DOCUMENT TYPE: Journal LANGUAGE: English

AB A practical method for the synthesis of bisphosphines containing homochiral C backbones, e.g., (2R,4R)-2,4-bis(dicyclohexylphosphino)pentane, is described. This procedure entails sequential reaction of a homochiral ditosylate, e.g., (2S,4S)-2,4-pentanediol di-p-toluenesulfonate, with the appropriate dialkyl- or diarylphosphine-borane anion,e.g., R2P·BH3-Li+ (e.g., R = cyclohexyl, Ph) followed by BH3 decomplexation

mediated by HBF4 OMe2.

RX(4) OF 92

L4 ANSWER 5 OF 6 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 123:112396 CASREACT <<LOGINID::20080512>>

TITLE: Process of preparing trimethylsilyloxy functionalized alkyllithium compounds

INVENTOR(S): alkyllithium compounds
Schwindeman, James A.

PATENT ASSIGNEE(S): FMC Corp., USA

SOURCE: U.S., 5 pp.
CODEN: USXXAM

DOCUMENT TYPE: Patent LANGUAGE: English

FAMILY ACC. NUM. COUNT: 2

PATENT INFORMATION:

P.F	PATENT NO.			KII	ND	DATE				APPLICATION NO.					DATE				
US	5 5	5435	540		Α			0806		US US	5 19 5 19	94-2 94-3	7972: 4182:	1 2	1994 1994 1995	1121			
	7	W:	GB,	GE, MN,	HU,	IS,	JP,	KE,	KG,	KP,	KR,	KZ,	LK,	LR,	DK, LŢ, SG,	LU,	LV,	MD,	
]	RW:	LU,		NL,										GB, GN,				
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	2 80	0052	25			L	2003						2,50	_					
	2 10	0504	1813	•	Т		1998 1999						05889 5132		1995 1997	-			
PRIORIT	ry <i>i</i>	APPI	LN.	INFO	.:					US WC	5 19 0 19	94-34 95-US	7972: 4182: 5925: 3719:	2 6	1994 1994 1995 1996	1121 0724			

OTHER SOURCE(S): MARPAT 123:112396

AB A process for producing compds. of the formula Me3SiORLi (R = C2-10 alkyl, C6-10 aryl) by reacting haloalc. HORX (R = same, X = C1, Br) with hexamethyldisilazane, in an inert atmospheric in hydrocarbon solvent, at a temperature

between 20° and reflux temperature of the solvent followed by lithiation with powdered lithium metal, is described. Thus, reaction of 3-chloro-2,2-dimethyl-1-propanol with hexamethyldisilazane in cyclohexane gave 3-chloro-2,2-dimethyl-1-trimethylsiloxypropane which on lithiation with lithium dispersion gave title compound, 3-chloro-2,2-dimethyl-1-trimethylsiloxypropyllithium.

RX(5) OF 9 $Me_{3}Si-O-(CH_{2})_{3}-C1 \qquad \underline{Li, Cyclohexane} \qquad Me_{3}Si-O-(CH_{2})_{3}-Li$ 9%

RX(6) OF 9
$$Me_{3}Si-O-(CH_{2})_{6}-C1 \qquad \underline{Li, Cyclohexane} \qquad \stackrel{Me_{3}Si-O-(CH_{2})_{6}-Li}{48}$$

$$RX(7)$$
 OF 9 - 2 STEPS

NOTE: 1) TMS-CL ADDED IN TWO BATCHES WITH HEATING BETWEEN ADDITIONS

RX(8) OF 9 - 2 STEPS

$$\begin{array}{c} \text{Me}_3\text{Si-NH-SiMe}_3 \\ & \xrightarrow{\text{Cyclohexane}} \\ & \xrightarrow{\text{L1. C1CH2CH2CH2OH,}} \\ & \xrightarrow{\text{Cyclohexane}} \\ & \xrightarrow{\text{Me}_3\text{Si-O-(CH}_2)}_3\text{-Li} \\ & \xrightarrow{\text{2. Li, Cyclohexane}} \\ \end{array}$$

NOTE: 1) TMS-CL ADDED IN TWO BATCHES WITH HEATING BETWEEN ADDITIONS

RX(9) OF 9 - 2 STEPS

Cl-(CH₂)₆-OH
$$\begin{array}{c} \text{1.1. (Me3Si) 2NH,} \\ \text{Cyclohexane} \\ \hline \text{1.2. Me3SiCl} \\ \text{2. Li, Cyclohexane} \end{array} \xrightarrow{\text{Me}_3\text{Si-O-}(\text{CH}_2)_6-\text{Li}} \\ 4\%$$

NOTE: 1) TMS-CL ADDED IN TWO BATCHES WITH HEATING BETWEEN ADDITIONS

L4 ANSWER 3 OF 6 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 136:232391 CASREACT <<LOGINID::20080512>>

TITLE: Chemical process and plant for n-butyl lithium

manufacture

INVENTOR(S): Buckley, Glyn Jeffrey; Stairmand, John William; Bowe,

Michael Joseph

PATENT ASSIGNEE(S): Accentus PLC, UK SOURCE: PCT Int. Appl., 15 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

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DATE
                                          APPLICATION NO.
                                                           DATE
    PATENT NO.
                     KIND
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                                       WO 2001-GB3982 20010905
    WO 2002020151
                     A1
                           20020314
            AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN,
            CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,
            HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,
            LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO,
            RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ,
            VN, YU, ZA, ZW
        RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY,
            DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF,
            BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
                                        AU 2001-84277
                                                           20010905
    AU 2001084277
                           20020322
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                                          EP 2001-963247
                                                           20010905
    EP 1320413
                           20030625
                      A1
                           20060405
    EP 1320413
                      В1
            AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
            IE, SI, LT, LV, FI, RO, MK, CY, AL, TR
                           20040318
                                          JP 2002-524623
                                                           20010905
     JP 2004508171
                      T
                                          US 2003-343786
    US 20030168330
                      Α1
                           20030911
                                                           20030204
                           20050111
    US 6841095
                      В2
                                          GB 2000-22016
PRIORITY APPLN. INFO.:
                                                           20000908
                                          WO 2001-GB3982
                                                           20010905
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AB A chemical plant for performing a chemical reaction between particles of a material such as lithium metal, and a reagent such as Bu chloride in solution in hexane, in which one reaction product is a solid material, includes a reaction vessel. Several ultrasonic transducers are attached to a wall of the vessel to irradiate ultrasonic waves into the vessel, the vessel being large enough that each transducer irradiates into fluid at least 0.1 m thick, each transducer irradiating no >3 W/cm2, and the transducers being sufficiently close to each other and the number of transducers being sufficiently high that the poser dissipation within the vessel is at least 10 W/L but no >200 W/L. The high intensity of ultrasound ensures that lithium chloride is cleaned off the surface of the lithium metal particles throughout the vessel.

RX(1) OF 1

H₃C-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-Li

NOTE: ultrasound, industrial scale, ultrasound is used to break the byproduct lithium chloride off of the lithium metal

L4 ANSWER 4 OF 6 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 129:149087 CASREACT <<LOGINID::20080512>>

TITLE: Preparation of alkyllithiums

INVENTOR(S): Iwao, Tetsuya; Yamamura, Kiyoshi

PATENT ASSIGNEE(S): Mitsui Petrochemical Industries, Ltd., Japan; Mitsui

Chemicals Inc.

SOURCE: Jpn. Kokai Tokkyo Koho, 3 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 10182658	A	19980707	JP 1996-345795	19961225
.TD 3570835	H2	20040929		

PRIORITY APPLN. INFO.: JP 1996-345795 19961225

AB Alkyllithiums are prepared by reaction of alkyl halides with Li containing ≤500 ppm N. BuCl was reacted with Li containing 160 ppm N in hexane at room temperature for 30-40 min, then filtered for 1 min to give 42% BuLi.

RX(1) OF 1

$$H_3C-CH_2-CH_2-CH_2-C1$$
 Li , Hexane, N2
 $H_3C-CH_2-CH_2-CH_2-CH_2-Li$

NOTE: room temp. 30-40 min